Tetrahedron Letters No. 1, pp 73 - 76.
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0040-4039/79/0101-0073$02.00/0

REACTIONS OF THE DIMETHYL CYCLOBUTANE-1,2-DICARBOXYLATE DIANION. A SIMPLE SYNTHESIS OF 1,2-DIHYDROCYCLOBUTA[b]NAPHTHALENE-3,8-DIONE

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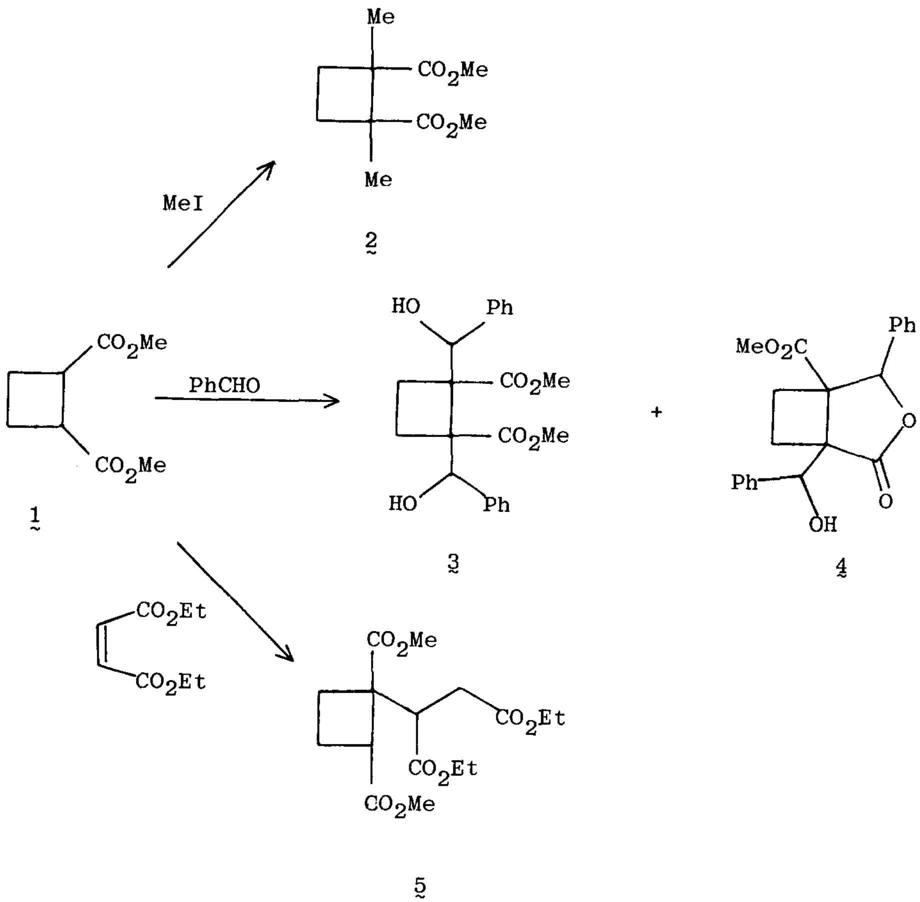
Vicinal diester dianions have considerable potential as synthetic intermediates, and we have recently described the formation and basicities of the dimethyl cyclobutane-1,2-dicarboxylate dianion (1) and the dimethyl cyclobut-3-ene-1,2-dicarboxylate dianion.[1] We now report some reactions of dianion 1 and outline a simple synthesis of 1,2-dihydrocyclobuta[b]naphthalene-3,8-dione (9),[2] a naphthoquinone annelated by a 4-membered ring, for which 1 serves as a precursor.

The dianion 1, prepared in THF with lithium diisopropylamide as previously described,[1] was reacted at -75 °C with 3 mole equivalents of CH_3I, when dimethyl 1,2-dimethylcyclobutane-1,2-dicarboxylate (2), 50 %, was isolated as a 4 : 1 mixture of isomers.[3,4] Reaction of 1 with 2 mole equivalents of benzaldehyde at -75 °C in THF gave a mixture (60 %) of the diester 3 [3] and the lactone 4 [3] upon aqueous workup and column chromatography. Both 3 and 4 are mixtures of stereomers, and these mixtures could be partially separated by chromatography and recrystallisation.[5]

The ready alkylation and acylation of the dianion encouraged us to investigate bis-addition to the anion as a method of annulation. However, reaction of 1 with 1,3-dibromopropane or o-phthalaldehyde gave only complex mixtures of products from which no cyclic material could be obtained.[6] Reaction of 1 with diethyl maleate at -80 °C in THF also did not give cyclic material, but in this case compound 5, resulting from a single Michael addition, could be isolated in 24 % yield.[3,4]

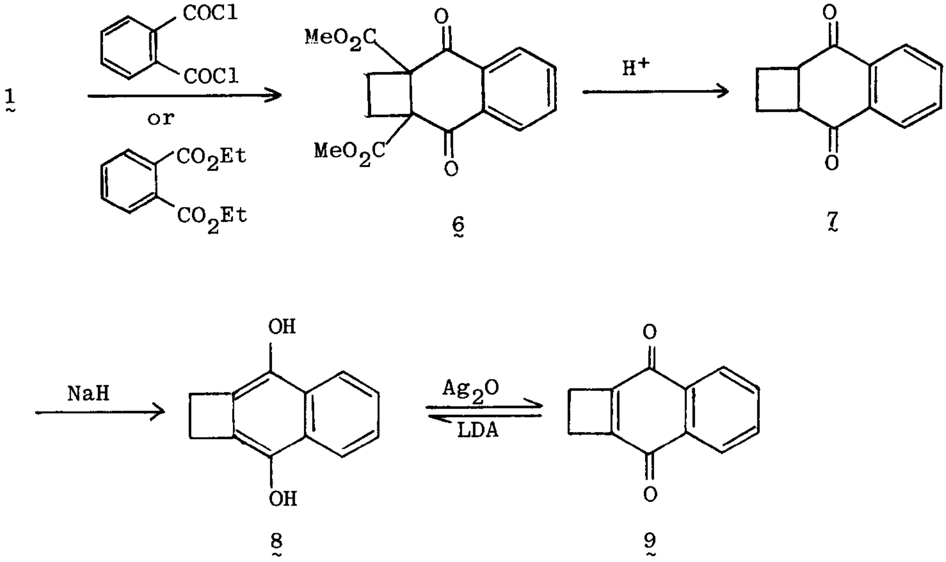
In contrast to these reactions, treatment of 1 with 1 mole equivalent of o-phthaloyl chloride gave the product of bis reaction, the dihydronaphthoquinone 6, albeit in low yield (∿ 5 %), and 6 could be obtained in much higher yield (54 %) by treatment of 1 with 2 mole equivalents of diethyl phthalate at -75 °C for 13 h. Compound 6, mp 134-146 °C,[3] showed

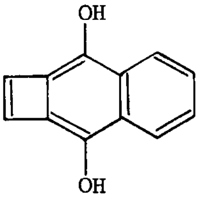


in the ^1H NMR spectrum ($CDCl_3$) signals at δ 8.36 - 7.72 (m, 4H), 3.74 (s, 6H) and 3.32 - 2.15 (m, 4H).

Heating 6 with a mixture of $CH_3CO_2H/H_2O/H_2SO_4$ (7 : 5 : 1) under reflux gave the dihydronaphthalene 7, mp 99 - 102 °C, 85 %, the ^1H NMR spectrum showing the expected changes.[3,4] Treatment of 7 with NaH in THF gave the hydroquinone 8, which on oxidation with Ag_2O gave the known quinone 9, mp 220 - 224 °C, (81 % 7 → 9), the observed spectral data being identical with those previously reported.[2,3,4] When compound 9 was treated with 3 mole equivalents of lithium diisopropylamide in THF/HMPA at -75 °C, the hydroquinone 8 was generated rather than the desired hydroquinone 11. LDA has previously been shown to act as a reducing agent with nonenolizable ketones.[7]

The synthesis of 9 from 1 illustrates the potential of vicinal diester dianions in





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organic synthesis. We are currently exploring both the further reactions of 1 and the dimethyl cyclobut-3-ene-1,2-dicarboxylate dianion, and also their higher cyclic homologues

ACKNOWLEDGEMENT

We thank the Science Research Council, U.K., for their support.

REFERENCES AND NOTES

1. P.J. Garratt and R. Zahler, J. Amer. Chem. Soc., accepted for publication.
2. M.P. Cava and R.L. Shirley, J. Org. Chem., **26**, 2212 (1961).
3. Satisfactory microanalytical and/or high resolution mass spectra data were obtained for this compound.
4. ^{1}H NMR, δ: **2** (2 isomers, CCl_4) 3.66, 3.58 (s, 4 : 1, 6H, OCH_3), 2.78 - 2.34 (m, 2H), 1.77 - 1.31 (m, 2H), 1.28, 1.25 (s, 1 : 4, 6H, CH_3); **5** (stereoisomeric mixture, CCl_4) 4.07 (br q, 4H), 3.64 (m, 6H, OCH_3), 3.38 - 1.71 (m, 8H), 1.18 (br t, 6H); **7** ($CDCl_3$) 8.29 - 7.65 (m, 4H), 3.88 - 3.49 (m, 2H), 2.90 - 2.20 (m, 4H); **8** ($(CD_3)_2CO$) 8.25 - 7.22 (m, 4H), 8.15 (s, 2H, OH), 3.16 (s, 4H); **9** ($CDCl_3$) 8.20 - 7.56 (m, 4H), 3.11 (s, 4H).
5. The ^{1}H NMR and I.R. spectra of the isolated isomers were consistent with the assigned structures.
6. The reaction of the cyclooctatetraenyl dianion with o-phthalaldehyde is also complex: T.S. Cantrell and H. Shechter, J. Amer. Chem. Soc., **89**, 5877 (1967).
7. C. Kowalski, X. Creary, A.J. Rollin, and M.C. Burke, J. Org. Chem., **43**, 2601 (1978).

(Received in UK 25 October 1978)